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Project Summary

ORIGINAL

Evaluation of Cryogenic Trapping as a Means for Collecting Organic Compounds in Ambient Air

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The methodology used in reduced temperature preconcentration of volatile organic compounds has been tested using a prototype automated gas chromatographic system. Mixtures of volatile organic compounds in humidified zero air were passed through a Nafion tube dryer and the organic compounds were collected on a reduced-temperature trap. The dryer reduced the water concentration without significantly affecting the integrity of the trace organic species. The selective reduction of water vapor improves the chromatography of the trace organics and likewise permits processing larger sample volumes.

Collection and recovery efficiencies of the volatile organic compounds at low ppbv levels (.3 to 3) were 100 ±5 percent with this preconcentration technique. The integrity of sample components was unaffected by co-collection of ozone and nitrogen dioxide at typical ambient concentrations. Two nominally identical automated gas chromatographic instruments were used for simultaneous monitoring of calibration mixtures and laboratory air. For calibration mixtures, percent relative errors were less than 10 percent over the concentration range of 0 to 50 ppbv for fourteen of the sixteen compounds; benzyl chloride and hexachlorobutadiene gave errors of 20 percent. For laboratory air analysis, deviation from the mean concentration for twenty-four comparisons ranged from 0.0 to 20.5 percent. Sixteen target compounds were stored at low ppb concentrations (2-5 ppbv) in passivated stainless steel containers and examined over a seven-day period. Statistical treatment of the data indicated that after four days of storage, measured concentrations for all sixteen compounds were within ±8 percent of the initial values. After seven days the average benzyl chloride concentration decreased by ~19 percent while hexachlorobutadiene increased by ~11 percent.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The atmosphere contains a complex mixture of organic compounds. Many of these emitted chemicals have been found to be highly toxic substances. Data on the identity and concentration levels of these compounds in urban and rural environments are continually being gathered by researchers who are attempting to better understand the chemistry and fate of these chemicals as well as the extent of human exposure to these compounds. From an analytical standpoint, this data gathering task has been formidable. However, these efforts have been dramatically improved in recent years through the use of capillary column gas chromatography coupled to compound-specific detection systems. Furthermore,

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the interfacing of the gas chromatograph to a mass spectrometer detector has permitted positive identification of many of these atmospheric constituents.

Most of these toxic chemicals are present at ppb levels or less and preconcentration is often necessary for accurate chemical analysis. Presently the two primary ambient air preconcentration techniques employed in delineating atmospheric organic burdens are cryogenic trapping and the use of solid adsorbents.

Cryogenic trapping can involve either of two collection procedures. With the first procedure, whole air samples are entirely condensed within suitable collection devices by cryogens such as liquid nitrogen or liquid helium. Both cryogens are sufficiently cool to serve as the cryogenic pump in this collection process. This approach is normally used in studies where remote sampling is being conducted. Once the sample is collected, the coolant is removed and the container returned to the laboratory for subsequent analysis.

The other cryogenic trapping procedure involves passing air through a reduced-temperature trap. At the appropriate temperature, trace organic species will condense onto the trap surfaces while oxygen and nitrogen pass through the system. Reduced-temperature trapping has several limitations which must be considered when designing a sampling and analytical system. A limiting factor of major importance is the co-collection of water in the sampling trap. One liter of air at 50 percent relative humidity and 25 C will contain approximately 10 mg of water, which appears as ice in the collection trap. The possibility of the ice plugging the trap and stopping sample flow is of concern, and water transferred to the gas chromatographic capillary column may also cause plugging and deleterious column effects. Furthermore, during sample preconcentration, chemical reactions may also occur in the collection trap. Possible reactants could include ammonia/acids, ozone/olefins, etc.

The Advanced Analysis Techniques Branch of the Environmental Monitoring Systems Laboratory (EMSL) is responsible for the development and evaluation of state-of-the-art and emerging analytical techniques for the determination of organic compounds in ambient air. Recently a priority listing of volatile organics has been established and the EMSL is focusing on further development of analytical methodology associated with the detection of these compounds. Primary emphasis has been placed on developing field-compatible analytical systems.

Recently a prototype automated analytical system incorporating cryogenic trapping for sample preconcentration has been developed jointly by EPA and the Battelle Columbus Laboratory. System hardware utilizes capillary column gas chromatographic separation techniques along with flame ionization and electron capture detection. Software development using the basic programming capability of the GC system permits calibration and ambient sampling to be achieved with minimal operator interfacing. In this report, we shall describe instrumentation hardware and software and shall discuss laboratory experiments designed to test the suitability of the prototype system for preconcentration of volatile organic compounds in ambient air. Table 1 lists the volatile organic compounds that were examined. The following laboratory studies were carried out during this program.

(1) A Perma-Pure dryer was tested to determine if water vapor could be selectively removed from the gas stream also containing the 16 target compounds without affecting the integrity of the organics in the gas phase.

(2) Collection and recovery efficiencies of the organic compounds were determined.

(3) Studies were also conducted with the target compounds to examine potential interference or artifact effects from co-collected ozone and nitrogen dioxide gases.

(4) A prototype calibration device was interfaced to the overall system and tested. Software was developed to permit automatic operation and calibration of the GC system.

(5) Side-by-side comparison of two prototype automated sampling and analysis units was carried out at the EPA facility. Calibration mixtures and ambient air samples were analyzed.

(6) In a joint effort with EPA, a comparison was made between analytical results for samples collected and temporarily stored in small metal cylinders, with data collected during real-time sampling.

Conclusions

During the laboratory experiments, two Nafion tube dryers were evaluated and found to reduce water vapor selectively in the gas phase without affecting the integrity of trace organic species also present. The selective reduction of water vapor improves the chromatographic resolution of the trace organics and likewise permits larger sample volumes to be processed. Experiments showed that collection and recovery efficiencies of the volatile organic compounds at low ppbv levels were 100 ± 5 percent with this preconcentration technique. Ozone and nitrogen dioxide interference studies indicated that none of the target compounds was affected by the additional presence of these reactive species. Furthermore, no artifact peaks or deleterious column effects were observed during or after these tests.

In a cooperative effort with EPA, two nominally identical automated GC systems were intercompared with calibration mixtures and ambient air samples drawn from a common manifold. Statistical analysis of the calibration data involved regressing concentration on raw area and determining the least squares regression line. A percent relative error of less than 10 was obtained for thirteen of the fifteen tested compounds when comparing the estimated concentration to the actual concentration. The remaining two compounds, benzyl chloride and hexachlorobutadiene, exhibited relative

Table 1. Volatile Organic Compounds Examined During Laboratory Studies

Propane	*Trichloroethylene*
Vinyl Chloride	*1,3-Dichloropropene (cis and trans)*
Vinylidene Chloride	*Toluene*
Trichlorotrifluoroethane	*1,2-Dibromoethane*
Chloroform	*Tetrachloroethylene*
1,2-Dichloroethane	*Chlorobenzene*
Methyl Chloroform	*o-Xylene*
Benzene	*Benzyl Chloride*
Carbon Tetrachloride	*Hexachlorobutadiene*

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error values of ~20 percent at the lowest non-zero concentration level (4 ppbv). Simultaneous sampling of laboratory air from a common manifold resulted in reasonable agreement between the two instruments. Nine target compounds were identified and quantified. The results indicated an overall precision of ±10 percent.

A test of the storage characteristics of passivated stainless steel canisters (seven) for a set of sixteen volatile organic compounds (2 to 5 ppbv) showed less than ±8 percent average change for all of the compounds over a four-day period. After seven days of storage, the average benzyl chloride concentration decreased by ~19 percent while hexachlorobutadiene increased by ~11 percent.

During the program, software was developed to more easily facilitate the monitoring and calibration needs of the automated GC sampling and analysis system. In addition to controlling zone heating and cooling, sample collection and injection, chromatographic run conditions and data processing, the developed software provided single point or multipoint calibration subroutines to be nested into the overall sampling and analysis strategy.

Recommendations

A gas chromatographic system employing reduced temperature preconcentration for the collection of VOC's has been laboratory tested with respect to sample drying procedures, co-collection of reactive ambient air species, and collection and release efficiency. An automated GC system has been used to more easily facilitate the laboratory tests.

The following recommendations are suggested:

- The automated GC system should be field tested. The two automated systems should be evaluated side-by-side during the first phase of the field program. Subsequently, the sample collection cycle would be offset so as to permit complete time coverage with both instruments. The cryogenic sampling system should also be compared with other preconcentration techniques such as solid adsorbents (Tenax, Carbosieve) and passive dosimeters. These tests would provide much needed information regarding the advantages and disadvantages of each technique.

- Many of the target compounds tested in this study will co-elute with other ambient air species. Although the combination of capillary column and flame ionization and electron capture detectors used in the current program help alleviate some of these concerns, other more selective detectors are needed. Integrating a mass-selective detector into the automated gas chromatographic system is recommended. The mass-selective detector offers both total ion and selected ion monitoring capability and will thus provide both qualitative and quantitative information. The increased specificity of this detector over other detection systems will allow better differentiation of co-eluting GC peaks and thus improve present quantitative capability.

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The complete report, entitled "Evaluation of Cryogenic Trapping as a Means for Collecting Organic Compounds in Ambient Air," (Order No. PB 85-144 046; Cost: $10.00, subject to change) will be available only from:
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